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* * * * * Welcome to STN International * * * * *

NEWS	1		Web Page for STN Seminar Schedule - N. America
NEWS	2	JUL 02	LMEDLINE coverage updated
NEWS	3	JUL 02	SCISEARCH enhanced with complete author names
NEWS	4	JUL 02	CHEMCATS accession numbers revised
NEWS	5	JUL 02	CA/CAPplus enhanced with utility model patents from China
NEWS	6	JUL 16	CAPplus enhanced with French and German abstracts
NEWS	7	JUL 18	CA/CAPplus patent coverage enhanced
NEWS	8	JUL 26	USPATFULL/USPAT2 enhanced with IPC reclassification
NEWS	9	JUL 30	USGENE now available on STN
NEWS	10	AUG 06	CAS REGISTRY enhanced with new experimental property tags
NEWS	11	AUG 06	FSTA enhanced with new thesaurus edition
NEWS	12	AUG 13	CA/CAPplus enhanced with additional kind codes for granted patents
NEWS	13	AUG 20	CA/CAPplus enhanced with CAS indexing in pre-1907 records
NEWS	14	AUG 27	Full-text patent databases enhanced with predefined patent family display formats from INPADOCDB
NEWS	15	AUG 27	USPATOLD now available on STN
NEWS	16	AUG 28	CAS REGISTRY enhanced with additional experimental spectral property data
NEWS	17	SEP 07	STN AnaVist, Version 2.0, now available with Derwent World Patents Index
NEWS	18	SEP 13	FORIS renamed to SOFIS
NEWS	19	SEP 13	INPADOCDB enhanced with monthly SDI frequency
NEWS	20	SEP 17	CA/CAPplus enhanced with printed CA page images from 1967-1998
NEWS	21	SEP 17	CAPplus coverage extended to include traditional medicine patents
NEWS	22	SEP 24	EMBASE, EMBAL, and LEMBASE reloaded with enhancements
NEWS	23	OCT 02	CA/CAPplus enhanced with pre-1907 records from Chemisches Zentralblatt
NEWS	24	OCT 19	BEILSTEIN updated with new compounds
NEWS	25	NOV 15	Derwent Indian patent publication number format enhanced
NEWS	26	NOV 19	WPIX enhanced with XML display format
NEWS	27	NOV 30	ICSD reloaded with enhancements
NEWS	28	DEC 04	LINPADOCDB now available on STN
NEWS EXPRESS	19	SEPTEMBER 2007: CURRENT WINDOWS VERSION IS V8.2, CURRENT MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP), AND CURRENT DISCOVER FILE IS DATED 19 SEPTEMBER 2007.	
NEWS HOURS		STN Operating Hours Plus Help Desk Availability	
NEWS LOGIN		Welcome Banner and News Items	
NEWS IPC8		For general information regarding STN implementation of IPC 8	

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* * * * * STN Columbus * * * * *

FILE 'HOME' ENTERED AT 11:02:48 ON 11 DEC 2007

=> file casreact

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

0.21

0.21

FILE 'CASREACT' ENTERED AT 11:03:05 ON 11 DEC 2007

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FILE CONTENT:1840 - 8 Dec 2007 VOL 147 ISS 25

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*
* CASREACT now has more than 13.8 million reactions *
*

Some CASREACT records are derived from the ZIC/VINITI database (1974-1999) provided by InfoChem, INPI data prior to 1986, and Biotransformations database compiled under the direction of Professor Dr. Klaus Kieslich.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=>

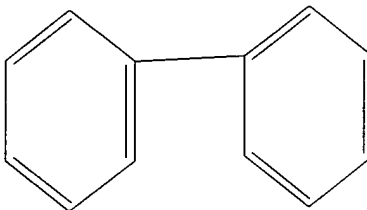
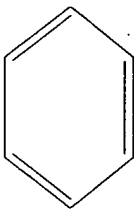
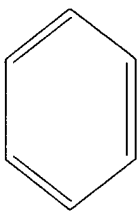
Uploading C:\Program Files\Stnexp\Queries\10812692.str

L1 STRUCTURE UPLOADED

=> d l1

L1 HAS NO ANSWERS

L1 STR



Structure attributes must be viewed using STN Express query preparation.

=> s l1
SAMPLE SEARCH INITIATED 11:03:32 FILE 'CASREACT'
SCREENING COMPLETE - 22923 REACTIONS TO VERIFY FROM 1600 DOCUMENTS

21.8% DONE 5000 VERIFIED 833 HIT RXNS 50 DOCS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.03

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED VERIFICATIONS: 449525 TO 467395
PROJECTED ANSWERS: 18333 TO 22087

L2 50 SEA SSS SAM L1 (833 REACTIONS)

=> s l1 full
FULL SEARCH INITIATED 11:03:39 FILE 'CASREACT'
SCREENING COMPLETE - 431843 REACTIONS TO VERIFY FROM 31093 DOCUMENTS

96.8% DONE 418233 VERIFIED 251099 HIT RXNS (3 INCOMP) 18536 DOCS
100.0% DONE 431843 VERIFIED 259332 HIT RXNS (3 INCOMP) 19361 DOCS
SEARCH TIME: 00.00.33

L3 19361 SEA SSS FUL L1 (259332 REACTIONS)

=> file caplus
COST IN U.S. DOLLARS SINCE FILE TOTAL
ENTRY SESSION
FULL ESTIMATED COST 114.00 114.21

FILE 'CAPLUS' ENTERED AT 11:04:20 ON 11 DEC 2007
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FILE COVERS 1907 - 11 Dec 2007 VOL 147 ISS 25
FILE LAST UPDATED: 10 Dec 2007 (20071210/ED)

Effective October 17, 2005, revised CAS Information Use Policies apply. They are available for your review at:

<http://www.cas.org/infopolicy.html>

=> s l3
L4 19364 L3

=> s l4 and oxidant
51422 OXIDANT
L5 153 L4 AND OXIDANT

=> s l5 and acid

```

      4496066 ACID
L6      56 L5 AND ACID

=> s 14 and quinone
      37604 QUINONE
L7      221 L4 AND QUINONE

=> s 14 and nitro?
      1234469 NITRO?
L8      3615 L4 AND NITRO?

=> s 18 or 17
L9      3802 L8 OR L7

=> s 19 and acid
      4496066 ACID
L10     1955 L9 AND ACID

=> s 110 and quenching
      132819 QUENCHING
L11     15 L10 AND QUENCHING

=> s 110 and quench?
      207486 QUENCH?
L12     17 L10 AND QUENCH?

=> s 16 and quench?
      207486 QUENCH?
L13     1 L6 AND QUENCH?

=> s 112 or 113
L14     17 L12 OR L13

=> s 114 not py > 2004
      3957356 PY > 2004
L15     9 L14 NOT PY > 2004

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```

=> s 115 ibib abd hitstr 1-
MISSING OPERATOR L15 IBIB
The search profile that was entered contains terms or
nested terms that are not separated by a logical operator.

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=> d 115 ibib abd hitstr 1-
'ABD' IS NOT A VALID FORMAT FOR FILE 'CAPLUS'

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The following are valid formats:

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ABS ----- GI and AB
ALL ----- BIB, AB, IND, RE
APPS ----- AI, PRAI
BIB ----- AN, plus Bibliographic Data and PI table (default)
CAN ----- List of CA abstract numbers without answer numbers
CBIB ----- AN, plus Compressed Bibliographic Data
CLASS ----- IPC, NCL, ECLA, FTERM
DALL ----- ALL, delimited (end of each field identified)
DMAX ----- MAX, delimited for post-processing
FAM ----- AN, PI and PRAI in table, plus Patent Family data
FBIB ----- AN, BIB, plus Patent FAM
IND ----- Indexing data
IPC ----- International Patent Classifications
MAX ----- ALL, plus Patent FAM, RE
PATS ----- PI, SO
SAM ----- CC, SX, TI, ST, IT

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SCAN ----- CC, SX, TI, ST, IT (random display, no answer numbers;
SCAN must be entered on the same line as the DISPLAY,
e.g., D SCAN or DISPLAY SCAN)

STD ----- BIB, CLASS

IABS ----- ABS, indented with text labels

IALL ----- ALL, indented with text labels

IBIB ----- BIB, indented with text labels

IMAX ----- MAX, indented with text labels

ISTD ----- STD, indented with text labels

OBIB ----- AN, plus Bibliographic Data (original)

OIBIB ----- OBIB, indented with text labels

SBIB ----- BIB, no citations

SIBIB ----- IBIB, no citations

HIT ----- Fields containing hit terms

HITIND ----- IC, ICA, ICI, NCL, CC and index field (ST and IT)
containing hit terms

HITRN ----- HIT RN and its text modification

HITSTR ----- HIT RN, its text modification, its CA index name, and
its structure diagram

HITSEQ ----- HIT RN, its text modification, its CA index name, its
structure diagram, plus NTE and SEQ fields

FHITSTR ----- First HIT RN, its text modification, its CA index name, and
its structure diagram

FHITSEQ ----- First HIT RN, its text modification, its CA index name, its
structure diagram, plus NTE and SEQ fields

KWIC ----- Hit term plus 20 words on either side

OCC ----- Number of occurrence of hit term and field in which it occurs

To display a particular field or fields, enter the display field codes. For a list of the display field codes, enter HELP DFIELDS at an arrow prompt (=>). Examples of formats include: TI; TI,AU; BIB,ST; TI,IND; TI,SO. You may specify the format fields in any order and the information will be displayed in the same order as the format specification.

All of the formats (except for SAM, SCAN, HIT, HITIND, HITRN, HITSTR, FHITSTR, HITSEQ, FHITSEQ, KWIC, and OCC) may be used with DISPLAY ACC to view a specified Accession Number.

ENTER DISPLAY FORMAT (BIB):exit
'EXIT' IS NOT A VALID FORMAT FOR FILE 'CAPLUS'

The following are valid formats:

ABS ----- GI and AB

ALL ----- BIB, AB, IND, RE

APPS ----- AI, PRAI

BIB ----- AN, plus Bibliographic Data and PI table (default)

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DMAX ----- MAX, delimited for post-processing

FAM ----- AN, PI and PRAI in table, plus Patent Family data

FBIB ----- AN, BIB, plus Patent FAM

IND ----- Indexing data

IPC ----- International Patent Classifications

MAX ----- ALL, plus Patent FAM, RE

PATS ----- PI, SO

SAM ----- CC, SX, TI, ST, IT

SCAN ----- CC, SX, TI, ST, IT (random display, no answer numbers;
 SCAN must be entered on the same line as the DISPLAY,
 e.g., D SCAN or DISPLAY SCAN)
 STD ----- BIB, CLASS

 IABS ----- ABS, indented with text labels
 IALL ----- ALL, indented with text labels
 IBIB ----- BIB, indented with text labels
 IMAX ----- MAX, indented with text labels
 ISTD ----- STD, indented with text labels

 OBIB ----- AN, plus Bibliographic Data (original)
 OIBIB ----- OBIB, indented with text labels

 SBIB ----- BIB, no citations
 SIBIB ----- IBIB, no citations

 HIT ----- Fields containing hit terms
 HITIND ----- IC, ICA, ICI, NCL, CC and index field (ST and IT)
 containing hit terms
 HITRN ----- HIT RN and its text modification
 HITSTR ----- HIT RN, its text modification, its CA index name, and
 its structure diagram
 HITSEQ ----- HIT RN, its text modification, its CA index name, its
 structure diagram, plus NTE and SEQ fields
 FHITSTR ----- First HIT RN, its text modification, its CA index name, and
 its structure diagram
 FHITSEQ ----- First HIT RN, its text modification, its CA index name, its
 structure diagram, plus NTE and SEQ fields
 KWIC ----- Hit term plus 20 words on either side
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All of the formats (except for SAM, SCAN, HIT, HITIND, HITRN, HITSTR,
 FHITSTR, HITSEQ, FHITSEQ, KWIC, and OCC) may be used with DISPLAY ACC
 to view a specified Accession Number.

ENTER DISPLAY FORMAT (BIB):abs
 YOU HAVE REQUESTED DATA FROM 9 ANSWERS - CONTINUE? Y/(N):n

=> d l15 ibib abs hitstr 1-
 YOU HAVE REQUESTED DATA FROM 9 ANSWERS - CONTINUE? Y/(N):y

L15 ANSWER 1 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 2005:17776 CAPLUS
 DOCUMENT NUMBER: 143:60031
 TITLE: Dialkylphosphinoimidazoles as new ligands for
 palladium-catalyzed coupling reactions of aryl
 chlorides
 AUTHOR(S): Harkal, Surendra; Rataboul, Franck; Zapf, Alexander;
 Fuhrmann, Christa; Riermeier, Thomas; Monsees, Axel;
 Beller, Matthias
 CORPORATE SOURCE: Leibniz-Institut fuer Organische Katalyse,
 Universitaet Rostock e.V., Rostock, 18055, Germany
 SOURCE: Advanced Synthesis & Catalysis (2004), 346(13-15),
 1742-1748
 CODEN: ASCAF7; ISSN: 1615-4150
 PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

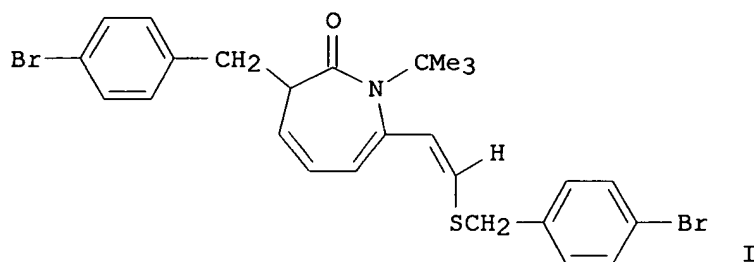
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 143:60031

AB 1-Aryl-2-(dialkylphosphino)-1H-imidazoles and -benzimidazoles were prepared and examined as ligands for palladium-catalyzed Suzuki coupling of aryl chlorides with phenylboronic acid. Imidazolylphosphines 1-Ar-2-PR₂-1H-imidazoles (1, 2, Ar = 2,4,6-Me₃C₆H₂, R = cyclohexyl, tBu) and 1-Ar-2-(PtBu₂)-1H-benzimidazoles (3, 4; Ar = Ph, 1-naphthyl) were conveniently prepared in one step from the corresponding heterocycles by selective deprotonation and quenching with corresponding ClPR₂. The novel ligands are easily tunable and show good to excellent performance in palladium-catalyzed Suzuki reactions of Ar₁Cl (Ar₁ = 4-MeC₆H₄, 4-MeCOC₆H₄, 4-CF₃C₆H₄, 4-MeOC₆H₄, 3-MeOC₆H₄, 2-MeC₆H₄, 2,6-Me₂C₆H₃, 3-pyridinyl) with phenylboronic acid, affording the corresponding biphenyls with 85-99% yield and 1900-8500 TON values. Buchwald-Hartwig amination of aryl substituted chlorobenzenes and 3-chloropyridine by primary and secondary aliphatic and aromatic amines gave corresponding arylamines with 68-99% yields.

REFERENCE COUNT: 71 THERE ARE 71 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 2 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2004:912880 CAPLUS
DOCUMENT NUMBER: 142:74399
TITLE: Dearomatizing rearrangements of lithiated thiophenecarboxamides
AUTHOR(S): Clayden, Jonathan; Turnbull, Rachel; Helliwell, Madeleine; Pinto, Ivan
CORPORATE SOURCE: Department of Chemistry, University of Manchester, Manchester, M13 9PL, UK
SOURCE: Chemical Communications (Cambridge, United Kingdom) (2004), (21), 2430-2431
CODEN: CHCOFS; ISSN: 1359-7345
PUBLISHER: Royal Society of Chemistry
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 142:74399
GI



AB Thiophene-3-carboxamides bearing allyl or benzyl substituents at nitrogen undergo dearomatizing cyclization on treatment with LDA. Rearrangements transform the dearomatized products into pyrrolinones, azepinones or partially saturated azepinothiophenes. E.g., deprotonation of N-allyl-N-tert-butylthiophene-3-carboxamide, followed by quenching with p-bromobenzyl bromide, gave 50% azepinone I.

REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 3 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2004:907016 CAPLUS

DOCUMENT NUMBER: 143:115215
TITLE: Polyazapodands derived from biphenyl. Study of their behavior as conformationally regulated fluorescent sensors
AUTHOR(S): Costero, Ana M.; Sanchis, Joaquin; Gil, Salvador; Sanz, Vicente; Ramirez de Arellano, M. Carmen; Gareth Williams, J. A.
CORPORATE SOURCE: Departament de Quimica Organica, Universitat de Valencia, Burjassot, 46100, Spain
SOURCE: Supramolecular Chemistry (2004), 16(6), 435-446
CODEN: SCHEER; ISSN: 1061-0278
PUBLISHER: Taylor & Francis Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 143:115215

AB Eight new polyazapodands containing a 4,4'-substituted biphenyl moiety have been synthesized. Four are functionalized on positions 4 and 4' with a nitro group and four with a dimethylamino substituent. Comparison of the emission behavior of clearly suggests that a modification in the dihedral angle between the biphenyl rings is an important factor in determining the fluorescent response of the mol. The fluorescence is pH dependent, due to the formation of intramol. hydrogen bonds between protonated aliphatic nitrogens and a carbonyl oxygen, which influences the aforementioned dihedral angle. A crystal structure resolved by X-ray diffraction, and confirms the dependence of the angle and the rigidity on the hydrogen bonding. The complexation properties of these ligands have been studied with Zn²⁺, Cd²⁺, Ni²⁺, Cu²⁺ and Pb²⁺, which show that the number of amino groups within the pendants has a strong influence on the nature of the complexation and the fluorescent response of each ligand.
REFERENCE COUNT: 20 THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 4 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2003:753346 CAPLUS
DOCUMENT NUMBER: 139:364494
TITLE: Photohydration and Photosolvolysis of Biphenyl Alkenes and Alcohols via Biphenyl Quinone Methide-type Intermediates and Diarylmethyl Carbocations
AUTHOR(S): Brousmiche, Darryl W.; Xu, Musheng; Lukeman, Matthew; Wan, Peter
CORPORATE SOURCE: Department of Chemistry, University of Victoria, Victoria, BC, V8W 3V6, Can.
SOURCE: Journal of the American Chemical Society (2003), 125(42), 12961-12970
CODEN: JACSAT; ISSN: 0002-7863
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 139:364494

AB Evidence is presented for the photochem. generation of novel biphenyl quinone methide (BQM)-type intermediates on photolysis of hydroxybiphenyl alkenes 7 and 8 [PhC(:CH₂)C₆H₄-4- and -3-C₆H₄OH-4, resp.] and hydroxybiphenyl alcs. 9 and 10 [PhCOH(Me)C₆H₄-4- and -3-C₆H₄OH-4, resp.]. Mechanistic investigations utilizing product, fluorescence, and nanosecond laser flash photolysis (LFP) studies indicate two distinct pathways for the formation of these BQMs depending upon the functional groups of the progenitor. Formal excited-state intramol. proton transfer (ESIPT) between the phenol and the alkene led to BQMs upon irradiation of the hydroxybiphenyl alkenes 7 and 8, while excited-state proton transfer (ESPT) to solvent followed by dehydroxylation was responsible for BQM formation from the hydroxybiphenyl alcs. 9 and 10. Photolysis of 7 and 8 in aqueous CH₃CN gave photohydration products via attack of water on the resp.

BQMs, while photolysis of the analogous Me ethers (of the phenolic moiety) gave only carbocation intermediates. Hydroxybiphenyl alcs. 9 and 10 yielded the corresponding photomethanolysis products in aqueous methanol, through attack of CH₃OH on the resp. BQMs. Although no evidence was found for BQM formation in LFP studies of 8 and 10, due to its suspected short lifetime, the resp. diaryl carbocation (λ_{max} 420 nm, τ = 8.5 μ s) has been observed upon irradiation of 8 in 2,2,2-trifluoroethanol. A BQM (λ_{max} 580 nm) was observed for 9 but not for 10, the latter having more complex chemical on laser excitation, resulting in a transient that appears to mask any BQM absorption. Significant quenching of fluorescence from the hydroxybiphenyl alkenes at low water content implies that H₂O is directly involved in reaction from the singlet excited state. The decrease in fluorescence intensity of 8 was found to depend on [H₂O]³; however, the distance required for ES IPT in these systems is too large to be bridged by a water trimer. The nonlinear quenching has been attributed to deprotonation of the phenol by two water mols., with concerted protonation at the alkene by another mol. of water. Fluorescence quenching of the hydroxybiphenyl alcs. required much higher water content, implying a different mechanism of reaction, consistent with the proposal of ESPT (to solvent water) followed by dehydroxylation.

REFERENCE COUNT: 36 THERE ARE 36 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 5 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2003:170641 CAPLUS

DOCUMENT NUMBER: 138:320857

TITLE: Host-[2]Rotaxane: Advantage of Converging Functional Groups for Guest Recognition

AUTHOR(S): Smukste, Inese; House, Brian E.; Smithrud, David B.

CORPORATE SOURCE: Department of Chemistry, University of Cincinnati, Cincinnati, OH, 45221-0172, USA

SOURCE: Journal of Organic Chemistry (2003), 68(7), 2559-2571
CODEN: JOCEAH; ISSN: 0022-3263

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 138:320857

AB A host-[2]rotaxane was constructed by converting a diaminophenylcalix[4]arene into a [2]rotaxane using the DCC-rotaxane method (Zehnder, D.; Smithrud, D. B.; Organic Lett. 2001, 16, 2485-2486). N-Ac-Arg groups were attached to the dibenzo-24-crown-8 ring of the rotaxane to provide a convergent functional group. To demonstrate the advantage provided by the rotaxane architecture for recognition of guests that contain a variety of functional groups, association consts. (K_A) for N-Ac-Trp, indole, N-Ac-Gly, fluorescein, 1-(dimethylamino)-5-naphthalenesulfonate, and pyrene bound to the [2]rotaxane were determined by performing ¹H NMR and fluorescence spectroscopic expts. The host-[2]rotaxane had the highest affinity for fluorescein with a K_A = 4.6 + 106 M⁻¹ in a 98/2 buffer (1 mM phosphate, pH 7)/DMSO solution. A comparison of K_A values demonstrates that both the aromatic pocket and ring of the host-[2]rotaxane contribute binding free energy for complexation. Association consts. were also derived for the same guests bound to the diaminophenylcalix[4]arene and to a diphenylcalix[4]arene that contained arginine residues displayed in a nonconvergent fashion. The host-[2]rotaxane provides higher affinity and specificity for most guests than the host with divergent N-Ac-Arg groups or the one that only has an aromatic pocket. For example, the K_A for the complex of the host-[2]rotaxane and fluorescein in the DMSO/water mixture is more than 2 orders of magnitude greater than association consts. derived for the other hosts.

REFERENCE COUNT: 55 THERE ARE 55 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 6 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2002:289507 CAPLUS
DOCUMENT NUMBER: 137:78680
TITLE: Stable ion and electrophilic chemistry of
fluoranthene-PAHs
AUTHOR(S): Laali, Kenneth K.; Okazaki, Takao; Galembeck, Sergio
E.
CORPORATE SOURCE: Department of Chemistry, Kent State University, Kent,
OH, 44242, USA
SOURCE: Journal of the Chemical Society, Perkin Transactions 2
(2002), (3), 621-629
CODEN: JCSPGI; ISSN: 1472-779X
PUBLISHER: Royal Society of Chemistry
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 137:78680

AB The first examples of persistent carbocations derived from parent
fluoranthene (four fused rings), benz[e]acephenanthrylene
(benzo[b]fluoranthene) (five fused rings) and its C-10 substituted derivs.
(X = OMe, F), as well as indeno[1,2,3-cd]pyrene (six fused rings) by
protonation with FSO₃H-SO₂ClF are reported. NMR characteristics (500 MHz)
of the resulting carbocations, their charge delocalization mode and
tropicity are examined. Relative arenium ion energies for all possible
protonation sites were calculated by AM1 for comparison with the NMR-based
assignments. The NMR chemical shifts for the observed arenium cations were
computed by GIAO-DFT calcns. at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level
(their energies and those of their neutral precursors were also calculated at
this level of theory). Relative aromaticity in various rings in the
resulting PAH-arenium ions was gauged via nucleus independent chemical shift
(NICS) calcns. It has been shown that the site of protonation and
nitration in 10-methoxybenz[e]acephenanthrylene are the same (C-9).
Quenching of the superacid solns. of fluoranthene and
10-methoxybenz[e]acephenanthrylene produced the dimers
3,3'-bifluoranthenyl and 10,10'-dimethoxy-9,9'-biacephenanthrenyl as minor
products (ca. 10% and ca. 33% resp.) in addition to the intact PAHs. It has
also been demonstrated that fluoranthene-PAHs and their derivs. are easily
protonated with [NH₄][NO₃] and observed in the gas phase via electrospray
mass spectrometry (ES-MS).

REFERENCE COUNT: 40 THERE ARE 40 CITED REFERENCES AVAILABLE FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 7 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2001:475265 CAPLUS
DOCUMENT NUMBER: 135:235356
TITLE: Metallocyclodextrins as Building Blocks in Noncovalent
Assemblies of Photoactive Units for the Study of
Photoinduced Intercomponent Processes
AUTHOR(S): Haider, Johanna M.; Chavarot, Murielle; Weidner,
Steffen; Sadler, Ian; Williams, Rene M.; De Cola,
Luisa; Pikramenou, Zoe
CORPORATE SOURCE: School of Chemistry, The University of Birmingham,
Edgbaston Birmingham, B15 2TT, UK
SOURCE: Inorganic Chemistry (2001), 40(16), 3912-3921
CODEN: INOCAJ; ISSN: 0020-1669
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 135:235356

AB Cyclodextrin cups were employed to build supramol. systems consisting of
metal and organic photoactive/redox-active components; the photoinduced
communication between redox-active units assembled in H₂O via noncovalent
interactions is established. The functionalization of a
β-cyclodextrin with a terpyridine unit, ttp-β-CD, is achieved by

protection of all but one of the hydroxyl groups by methylation and attachment of the ttp unit on the free primary hydroxyl group. The metalloreceptors $[(\beta\text{-CD-ttp})\text{Ru(ttp)}][\text{PF}_6]_2$, $[(\beta\text{-CD-ttp})\text{Ru(tpy)}][\text{PF}_6]_2$, and $[\text{Ru}(\beta\text{-CD-ttp})_2][\text{PF}_6]_2$ were synthesized and fully characterized. The $[(\beta\text{-CD-ttp})\text{Ru(ttp)}][\text{PF}_6]_2$ metalloreceptor exhibits luminescence in H_2O , centered at 640 nm, from the 3MLCT state with a lifetime of 1.9 ns and a quantum yield of $\Phi = 4.1 \times 10^{-5}$. Addition of redox-active quinone guests AQS, AQC, and BQ to an aqueous solution of $[(\beta\text{-CD-ttp})\text{Ru(ttp)}]^{2+}$ results in quenching of the luminescence up to 40%, 20%, and 25%, resp. Measurement of the binding strength indicates that, in saturation conditions, 85% for AQS and 77% for AQC are bound. The luminescence quenching is attributed to an intercomponent electron transfer from the appended Ru center to the quinone guest inside the cavity. Control expts. demonstrate no bimol. quenching at these conditions. A photoactive Os metalloguest, $[\text{Os}(\text{biptpy})(\text{tpy})][\text{PF}_6]$, is designed with a biphenyl hydrophobic tail for insertion in the cyclodextrin cavity. The complex is luminescent at room temperature with an emission band maximum at 730 nm and a lifetime of 116 ns. The Os(III) species are formed for the study of photoinduced electron transfer upon their assembly with the Ru cyclodextrin, $[(\beta\text{-CD-ttp})\text{Ru(ttp)}]^{2+}$. Time-resolved spectroscopy studies show a short component of 10 ps, attributed to electron transfer from Ru(II) to Os(III) giving an electron transfer rate 9.5×10^9 s⁻¹.

REFERENCE COUNT: 72 THERE ARE 72 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 8 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1985:148586 CAPLUS

DOCUMENT NUMBER: 102:148586

TITLE: Photophysical studies on 1-(p-aminophenyl)pyrene. Characterization of an intramolecular charge-transfer state with application to proton-transfer dynamics

AUTHOR(S): Hagopian, Sair; Singer, Lawrence A.

CORPORATE SOURCE: Dep. Chem., Univ. South. California, Los Angeles, CA, 90089-1062, USA

SOURCE: Journal of the American Chemical Society (1985), 107(7), 1874-80

CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 102:148586

AB A photophys. study on 1-(p-aminophenyl)pyrene (I) reveals 2 principal fluorescences arising from π, π^* (locally excited in pyrene ring) and charge-transfer (CT) (PhNH_2 as donor, pyrene as acceptor) states. The latter of the CT states in highly polar solvents (.apprx.500 nm, .apprx.2.5 eV) agrees well with the measured redox energetics (2.7 eV) while the dependence of the transition of .apprx.14 D. The photophysics of I is pH dependent in aqueous media because of conjugate acid-base equilibrium, with ground- and excited-state consts. of $\text{pK}_a = 4.05$, $\text{pK}_a^* = 3.3$ (Forster cycle), resp., in 1:1 EtOH- H_2O . The rather similar acidities of the ground and excited states of I indicate little or no CT contribution to the excited-state deprotonation. Deprotonation of the locally excited π, π^* state of I conjugate acid yields initially the locally excited free-base form of I, which rapidly relaxes to the CT state. The latter is subject to proton-transfer quenching (most likely via the pyrene radical-anion moiety of the CT state), $k_q = (7.38 \pm 1.5) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (corrected for changing proton activity coeffs. in EtOH- H_2O). Study of the rate of deprotonation of the conjugate acid of I* from room temperature through the liquid-solid phase transition (near -50°) to -196° allows an estimate of the enthalpy and entropy of activation in several different regions. As the temperature is lowered from 295 to 160 K, the enthalpy term decreases from 5360 to 780

cal/mol while the entropy term changes from -6.1 to -24.3 cal/K.mol).

L15 ANSWER 9 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1961:43315 CAPLUS

DOCUMENT NUMBER: 55:43315

ORIGINAL REFERENCE NO.: 55:8429e-i,8430a-c

TITLE: Quinones. XXXIII. Condensation of aryl naphthoquinones with sodium enolates of acetoacetic and malonic esters and their analogs

AUTHOR(S): Grinev, A. N.; Mezentshev, A. S.; Terent'ev, A. P.

CORPORATE SOURCE: State Univ., Moscow

SOURCE: Zhurnal Obshchei Khimii (1960), 30, 2306-11

CODEN: ZOKHA4; ISSN: 0044-460X

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

OTHER SOURCE(S): CASREACT 55:43315

GI For diagram(s), see printed CA Issue.

AB cf. CA 54, 10970c; 55, 6453h. The $\text{AcCHNaCO}_2\text{Et}$ from 13 g. $\text{AcCH}_2\text{CO}_2\text{Et}$ and 2.3 g. Na in dioxane was treated over 1 hr. with 23.4 g. 2-phenyl-1,4-naphthoquinone in dioxane with ice-cooling, the mixture kept 1 hr. at room temperature, 20 ml. H_2O added, a stream of air blown through the mixture 1.5 hrs., the mixture quenched in ice-HCl, and extracted with Et_2O to give 30% Et 2-phenyl-1,4-naphthoquinon-3-ylacetoacetate, m. 121-3°, and 5% Et₂O-insol. I, m. 182-4°. No products of the latter type were isolated from the subsequent reactions. If the above mixture was heated with 98% AcOH containing a trace of H_2SO_4 1.5 hrs., the product was 61% 2-methyl-3-carbethoxy-4-phenyl-5-hydroxynaphthofuran (Ia), m. 122-4°. Condensation of $\text{AcCH}_2\text{CO}_2\text{Et}$ or $\text{BzCH}_2\text{CO}_2\text{Et}$ with the appropriate 2-aryl-1,4-naphthoquinone as above gave: Et 2-(p-nitrophenyl)-1,4-naphthoquinon-3-ylacetoacetate, m. 195-7°, 52%; Et 2-phenyl-1,4-naphthoquinon-3-ylbenzoylacetate (II), m. 130-2°, 40%; Et 2-(p-nitrophenyl)-1,4-naphthoquinon-3-ylbenzoylacetate, m. 209-10°, 45%; Et 2-phenyl-1,4-naphthoquinon-3-yl(p-nitrobenzoyl)acetate, m. 138-40°, 55%; Et 2-phenyl-1,4-naphthoquinon-3-yl(p-chlorobenzoyl)acetate, m. 133-5°, 37%. II with aqueous $\text{Na}_2\text{S}_2\text{O}_4$ gave 88% 2,4-diphenyl-3-carbethoxy-5-hydroxynaphthofuran, m. 128-9°; similarly was prepared 87% 2-(p-nitrophenyl)-3-carbethoxy-4-phenyl-4-hydroxynaphthofuran, m. 226-8°. To $\text{AcCHNaCO}_2\text{Et}$, from 22 g. ester, prepared in absolute EtOH, was added at 0° 11.7 g. 2-phenyl-1,4-naphthoquinone in dry dioxane, followed by 20 ml. H_2O , and the whole kept 1 hr. at 50° to yield after acidification 65% I. Reaction of malonic ester with Na in dioxane, followed by treatment with 2-phenyl-1,4-naphthoquinone, as above, gave 50% 2,5-dihydroxy-4-phenyl naphthofuran, m. 195-7°. Shaking Ia with 2N NaOH and Me_2SO_4 in dioxane 1 hr. gave 95% 5-methoxy analog (III) of Ia, m. 122-3°. Similarly was prepared 2,4-diphenyl-3-carbethoxy-5-methoxynaphthofuran m. 106-7°, and 2-(p-nitrophenyl)-3-carbethoxy-4-phenyl-5-methoxynaphthofuran, m. 201-2°. III refluxed with alc. NaOH 4 hrs. gave on acidification 2-methyl-3-carboxy-4-phenyl-5-methoxynaphthofuran, m. 214-16°, which treated with SOCl_2 in CCl_4 at 40° then AlCl_3 at 0° 1 hr. and at room temperature 3 hrs. gave after quenching in ice-HCl 30% IV, m. 174-6°.

=> d l15 ibib abs tot 1-

YOU HAVE REQUESTED DATA FROM 18 ANSWERS - CONTINUE? Y/(N):y

L15 ANSWER 1 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

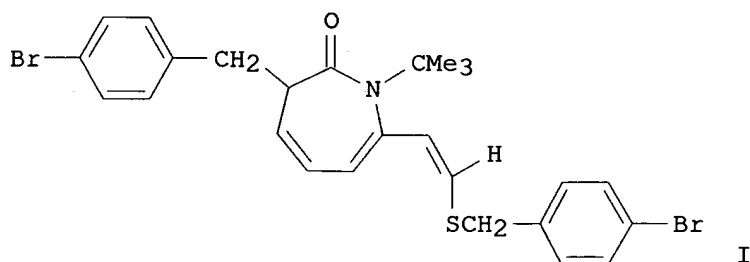
ACCESSION NUMBER: 2005:17776 CAPLUS

DOCUMENT NUMBER: 143:60031

TITLE: Dialkylphosphinoimidazoles as new ligands for palladium-catalyzed coupling reactions of aryl

chlorides
 AUTHOR(S): Harkal, Surendra; Rataboul, Franck; Zapf, Alexander; Fuhrmann, Christa; Riermeier, Thomas; Monsees, Axel; Beller, Matthias
 CORPORATE SOURCE: Leibniz-Institut fuer Organische Katalyse, Universitaet Rostock e.V., Rostock, 18055, Germany
 SOURCE: Advanced Synthesis & Catalysis (2004), 346(13-15), 1742-1748
 CODEN: ASCAF7; ISSN: 1615-4150
 PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 143:60031
 AB 1-Aryl-2-(dialkylphosphino)-1H-imidazoles and -benzimidazoles were prepared and examined as ligands for palladium-catalyzed Suzuki coupling of aryl chlorides with phenylboronic acid. Imidazolylphosphines 1-Ar-2-PR₂-1H-imidazoles (1, 2, Ar = 2,4,6-Me₃C₆H₂, R = cyclohexyl, tBu) and 1-Ar-2-(PtBu₂)-1H-benzimidazoles (3, 4; Ar = Ph, 1-naphthyl) were conveniently prepared in one step from the corresponding heterocycles by selective deprotonation and quenching with corresponding ClPR₂. The novel ligands are easily tunable and show good to excellent performance in palladium-catalyzed Suzuki reactions of Ar₁Cl (Ar₁ = 4-MeC₆H₄, 4-MeCOC₆H₄, 4-CF₃C₆H₄, 4-MeOC₆H₄, 3-MeOC₆H₄, 2-MeC₆H₄, 2,6-Me₂C₆H₃, 3-pyridinyl) with phenylboronic acid, affording the corresponding biphenyls with 85-99% yield and 1900-8500 TON values. Buchwald-Hartwig amination of aryl substituted chlorobenzenes and 3-chloropyridine by primary and secondary aliphatic and aromatic amines gave corresponding arylamines with 68-99% yields.
 REFERENCE COUNT: 71 THERE ARE 71 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 2 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN
 ACCESSION NUMBER: 2004:912880 CAPLUS
 DOCUMENT NUMBER: 142:74399
 TITLE: Dearomatizing rearrangements of lithiated thiophenecarboxamides
 AUTHOR(S): Clayden, Jonathan; Turnbull, Rachel; Helliwell, Madeleine; Pinto, Ivan
 CORPORATE SOURCE: Department of Chemistry, University of Manchester, Manchester, M13 9PL, UK
 SOURCE: Chemical Communications (Cambridge, United Kingdom) (2004), (21), 2430-2431
 CODEN: CHCOFS; ISSN: 1359-7345
 PUBLISHER: Royal Society of Chemistry
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 142:74399
 GI



AB Thiophene-3-carboxamides bearing allyl or benzyl substituents at

nitrogen undergo dearomatizing cyclization on treatment with LDA. Rearrangements transform the dearomatized products into pyrrolinones, azepinones or partially saturated azepinothiophenes. E.g., deprotonation of N-allyl-N-tert-butylthiophene-3-carboxamide, followed by quenching with p-bromobenzyl bromide, gave 50% azepinone I.

REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 3 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2004:907016 CAPLUS

DOCUMENT NUMBER: 143:115215

TITLE: Polyazapodands derived from biphenyl. Study of their behavior as conformationally regulated fluorescent sensors

AUTHOR(S): Costero, Ana M.; Sanchis, Joaquin; Gil, Salvador; Sanz, Vicente; Ramirez de Arellano, M. Carmen; Gareth Williams, J. A.

CORPORATE SOURCE: Departament de Quimica Organica, Universitat de Valencia, Burjassot, 46100, Spain

SOURCE: Supramolecular Chemistry (2004), 16(6), 435-446
CODEN: SCHEER; ISSN: 1061-0278

PUBLISHER: Taylor & Francis Ltd.

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 143:115215

AB Eight new polyazapodands containing a 4,4'-substituted biphenyl moiety have been synthesized. Four are functionalized on positions 4 and 4' with a nitro group and four with a dimethylamino substituent. Comparison of the emission behavior of clearly suggests that a modification in the dihedral angle between the biphenyl rings is an important factor in determining the fluorescent response of the mol. The fluorescence is pH dependent, due to the formation of intramol. hydrogen bonds between protonated aliphatic nitrogens and a carbonyl oxygen, which influences the aforementioned dihedral angle. A crystal structure resolved by X-ray diffraction, and confirms the dependence of the angle and the rigidity on the hydrogen bonding. The complexation properties of these ligands have been studied with Zn²⁺, Cd²⁺, Ni²⁺, Cu²⁺ and Pb²⁺, which show that the number of amino groups within the pendants has a strong influence on the nature of the complexation and the fluorescent response of each ligand.

REFERENCE COUNT: 20 THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 4 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2003:753346 CAPLUS

DOCUMENT NUMBER: 139:364494

TITLE: Photohydration and Photosolvolysis of Biphenyl Alkenes and Alcohols via Biphenyl Quinone Methide-type Intermediates and Diarylmethyl Carbocations

AUTHOR(S): Brousmiche, Darryl W.; Xu, Musheng; Lukeman, Matthew; Wan, Peter

CORPORATE SOURCE: Department of Chemistry, University of Victoria, Victoria, BC, V8W 3V6, Can.

SOURCE: Journal of the American Chemical Society (2003), 125(42), 12961-12970
CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 139:364494

AB Evidence is presented for the photochem. generation of novel biphenyl quinone methide (BQM)-type intermediates on photolysis of hydroxybiphenyl alkenes 7 and 8 [PhC(:CH₂)C₆H₄-4- and -3-C₆H₄OH-4, resp.]

and hydroxybiphenyl alcs. 9 and 10 [PhCOH(Me)C₆H₄-4- and -3-C₆H₄OH-4, resp.]. Mechanistic investigations utilizing product, fluorescence, and nanosecond laser flash photolysis (LFP) studies indicate two distinct pathways for the formation of these BQMs depending upon the functional groups of the progenitor. Formal excited-state intramol. proton transfer (ESIPT) between the phenol and the alkene led to BQMs upon irradiation of the hydroxybiphenyl alkenes 7 and 8, while excited-state proton transfer (ESPT) to solvent followed by dehydroxylation was responsible for BQM formation from the hydroxybiphenyl alcs. 9 and 10. Photolysis of 7 and 8 in aqueous CH₃CN gave photohydration products via attack of water on the resp. BQMs, while photolysis of the analogous Me ethers (of the phenolic moiety) gave only carbocation intermediates. Hydroxybiphenyl alcs. 9 and 10 yielded the corresponding photomethanolysis products in aqueous methanol, through attack of CH₃OH on the resp. BQMs. Although no evidence was found for BQM formation in LFP studies of 8 and 10, due to its suspected short lifetime, the resp. diaryl carbocation (λ_{max} 420 nm, τ = 8.5 μ s) has been observed upon irradiation of 8 in 2,2,2-trifluoroethanol. A BQM (λ_{max} 580 nm) was observed for 9 but not for 10, the latter having more complex chemical on laser excitation, resulting in a transient that appears to mask any BQM absorption. Significant quenching of fluorescence from the hydroxybiphenyl alkenes at low water content implies that H₂O is directly involved in reaction from the singlet excited state. The decrease in fluorescence intensity of 8 was found to depend on [H₂O]³; however, the distance required for ESIPT in these systems is too large to be bridged by a water trimer. The nonlinear quenching has been attributed to deprotonation of the phenol by two water mols., with concerted protonation at the alkene by another mol. of water. Fluorescence quenching of the hydroxybiphenyl alcs. required much higher water content, implying a different mechanism of reaction, consistent with the proposal of ESPT (to solvent water) followed by dehydroxylation.

REFERENCE COUNT: 36 THERE ARE 36 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 5 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2003:170641 CAPLUS

DOCUMENT NUMBER: 138:320857

TITLE: Host-[2]Rotaxane: Advantage of Converging Functional Groups for Guest Recognition

AUTHOR(S): Smukste, Inese; House, Brian E.; Smithrud, David B.

CORPORATE SOURCE: Department of Chemistry, University of Cincinnati, Cincinnati, OH, 45221-0172, USA

SOURCE: Journal of Organic Chemistry (2003), 68(7), 2559-2571
CODEN: JOCEAH; ISSN: 0022-3263

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 138:320857

AB A host-[2]rotaxane was constructed by converting a diaminophenylcalix[4]arene into a [2]rotaxane using the DCC-rotaxane method (Zehnder, D.; Smithrud, D. B.; Organic Lett. 2001, 16, 2485-2486). N-Ac-Arg groups were attached to the dibenzo-24-crown-8 ring of the rotaxane to provide a convergent functional group. To demonstrate the advantage provided by the rotaxane architecture for recognition of guests that contain a variety of functional groups, association consts. (K_A) for N-Ac-Trp, indole, N-Ac-Gly, fluorescein, 1-(dimethylamino)-5-naphthalenesulfonate, and pyrene bound to the [2]rotaxane were determined by performing ¹H NMR and fluorescence spectroscopic expts. The host-[2]rotaxane had the highest affinity for fluorescein with a K_A = 4.6 + 106 M⁻¹ in a 98/2 buffer (1 mM phosphate, pH 7)/DMSO solution. A comparison of K_A values demonstrates that both the aromatic pocket and ring of the host-[2]rotaxane contribute binding free energy for complexation. Association consts. were also derived for the same guests bound to the

diaminophenylcalix[4]arene and to a diphenylcalix[4]arene that contained arginine residues displayed in a nonconvergent fashion. The host-[2]rotaxane provides higher affinity and specificity for most guests than the host with divergent N-Ac-Arg groups or the one that only has an aromatic pocket. For example, the KA for the complex of the host-[2]rotaxane and fluorescein in the DMSO/water mixture is more than 2 orders of magnitude greater than association consts. derived for the other hosts.

REFERENCE COUNT: 55 THERE ARE 55 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 6 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2002:289507 CAPLUS

DOCUMENT NUMBER: 137:78680

TITLE: Stable ion and electrophilic chemistry of fluoranthene-PAHs

AUTHOR(S): Laali, Kenneth K.; Okazaki, Takao; Galembeck, Sergio E.

CORPORATE SOURCE: Department of Chemistry, Kent State University, Kent, OH, 44242, USA

SOURCE: Journal of the Chemical Society, Perkin Transactions 2 (2002), (3), 621-629
CODEN: JCSPGI; ISSN: 1472-779X

PUBLISHER: Royal Society of Chemistry

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 137:78680

AB The first examples of persistent carbocations derived from parent fluoranthene (four fused rings), benz[e]acephenanthrylene (benzo[b]fluoranthene) (five fused rings) and its C-10 substituted derivs. (X = OMe, F), as well as indeno[1,2,3-cd]pyrene (six fused rings) by protonation with FSO₃H-SO₂ClF are reported. NMR characteristics (500 MHz) of the resulting carbocations, their charge delocalization mode and tropicity are examined. Relative arenium ion energies for all possible protonation sites were calculated by AM1 for comparison with the NMR-based assignments. The NMR chemical shifts for the observed arenium cations were computed by GIAO-DFT calcns. at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level (their energies and those of their neutral precursors were also calculated at this level of theory). Relative aromaticity in various rings in the resulting PAH-arenium ions was gauged via nucleus independent chemical shift (NICS) calcns. It has been shown that the site of protonation and nitration in 10-methoxybenz[e]acephenanthrylene are the same (C-9). Quenching of the superacid solns. of fluoranthene and 10-methoxybenz[e]acephenanthrylene produced the dimers 3,3'-bifluoranthenyl and 10,10'-dimethoxy-9,9'-biacephenanthrenyl as minor products (ca. 10% and ca. 33% resp.) in addition to the intact PAHs. It has also been demonstrated that fluoranthene-PAHs and their derivs. are easily protonated with [NH₄][NO₃] and observed in the gas phase via electrospray mass spectrometry (ES-MS).

REFERENCE COUNT: 40 THERE ARE 40 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 7 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2001:475265 CAPLUS

DOCUMENT NUMBER: 135:235356

TITLE: Metallocyclodextrins as Building Blocks in Noncovalent Assemblies of Photoactive Units for the Study of Photoinduced Intercomponent Processes

AUTHOR(S): Haider, Johanna M.; Chavarot, Murielle; Weidner, Steffen; Sadler, Ian; Williams, Rene M.; De Cola, Luisa; Pikramenou, Zoe

CORPORATE SOURCE: School of Chemistry, The University of Birmingham, Edgbaston Birmingham, B15 2TT, UK

SOURCE: Inorganic Chemistry (2001), 40(16), 3912-3921

PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 135:235356

AB Cyclodextrin cups were employed to build supramol. systems consisting of metal and organic photoactive/redox-active components; the photoinduced communication between redox-active units assembled in H₂O via noncovalent interactions is established. The functionalization of a β -cyclodextrin with a terpyridine unit, ttp- β -CD, is achieved by protection of all but one of the hydroxyl groups by methylation and attachment of the ttp unit on the free primary hydroxyl group. The metalloreceptors [(β -CD-ttp)Ru(ttp)][PF₆]₂, [(β -CD-ttp)Ru(tpy)][PF₆]₂, and [Ru(β -CD-ttp)₂][PF₆]₂ were synthesized and fully characterized. The [(β -CD-ttp)Ru(ttp)][PF₆]₂ metalloreceptor exhibits luminescence in H₂O, centered at 640 nm, from the 3MLCT state with a lifetime of 1.9 ns and a quantum yield of $\Phi = 4.1 \times 10^{-5}$. Addition of redox-active quinone guests AQS, AQC, and BQ to an aqueous solution of [(β -CD-ttp)Ru(ttp)]²⁺ results in quenching of the luminescence up to 40%, 20%, and 25%, resp. Measurement of the binding strength indicates that, in saturation conditions, 85% for AQS and 77% for AQC are bound. The luminescence quenching is attributed to an intercomponent electron transfer from the appended Ru center to the quinone guest inside the cavity. Control expts. demonstrate no bimol. quenching at these conditions. A photoactive Os metalloguest, [Os(biptpy)(tpy)][PF₆], is designed with a biphenyl hydrophobic tail for insertion in the cyclodextrin cavity. The complex is luminescent at room temperature with an emission band maximum at 730 nm and a lifetime of 116 ns. The Os(III) species are formed for the study of photoinduced electron transfer upon their assembly with the Ru cyclodextrin, [(β -CD-ttp)Ru(ttp)]²⁺. Time-resolved spectroscopy studies show a short component of 10 ps, attributed to electron transfer from Ru(II) to Os(III) giving an electron transfer rate 9.5×10^9 s⁻¹.

REFERENCE COUNT: 72 THERE ARE 72 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 8 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1985:148586 CAPLUS
DOCUMENT NUMBER: 102:148586
TITLE: Photophysical studies on 1-(p-aminophenyl)pyrene. Characterization of an intramolecular charge-transfer state with application to proton-transfer dynamics
AUTHOR(S): Hagopian, Sair; Singer, Lawrence A.
CORPORATE SOURCE: Dep. Chem., Univ. South. California, Los Angeles, CA, 90089-1062, USA
SOURCE: Journal of the American Chemical Society (1985), 107(7), 1874-80
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 102:148586

AB A photophys. study on 1-(p-aminophenyl)pyrene (I) reveals 2 principal fluorescences arising from π, π^* (locally excited in pyrene ring) and charge-transfer (CT) (PhNH₂ as donor, pyrene as acceptor) states. The latter of the CT states in highly polar solvents (.apprx.500 nm, .apprx.2.5 eV) agrees well with the measured redox energetics (2.7 eV) while the dependence of the transition of .apprx.14 D. The photophysics of I is pH dependent in aqueous media because of conjugate acid-base equilibrium, with ground- and excited-state consts. of pK_a = 4.05, pK_a^{*} = 3.3 (Forster cycle), resp., in 1:1 EtOH-H₂O. The rather similar acidities of the ground and excited states of I indicate little or no CT contribution to the excited-state deprotonation. Deprotonation of the locally excited

π, π^* state of I conjugate acid yields initially the locally excited free-base form of I, which rapidly relaxes to the CT state. The latter is subject to proton-transfer quenching (most likely via the pyrene radical-anion moiety of the CT state), $k_q = (7.38 \pm 1.5) + 108 \text{ M}^{-1} \text{ s}^{-1}$ (corrected for changing proton activity coeffs. in EtOH-H₂O). Study of the rate of deprotonation of the conjugate acid of I* from room temperature through the liquid-solid phase transition (near -50°) to -196° allows an estimate of the enthalpy and entropy of activation in several different regions. As the temperature is lowered from 295 to 160 K, the enthalpy term decreases from 5360 to 780 cal/mol while the entropy term changes from -6.1 to -24.3 cal/K·mol).

L15 ANSWER 9 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1961:43315 CAPLUS
 DOCUMENT NUMBER: 55:43315
 ORIGINAL REFERENCE NO.: 55:8429e-i,8430a-c
 TITLE: Quinones. XXXIII. Condensation of aryl naphthoquinones with sodium enolates of acetoacetic and malonic esters and their analogs
 AUTHOR(S): Grinev, A. N.; Mezentshev, A. S.; Terent'ev, A. P.
 CORPORATE SOURCE: State Univ., Moscow
 SOURCE: Zhurnal Obshchei Khimii (1960), 30, 2306-11
 CODEN: ZOKHA4; ISSN: 0044-460X
 DOCUMENT TYPE: Journal
 LANGUAGE: Unavailable
 OTHER SOURCE(S): CASREACT 55:43315

GI For diagram(s), see printed CA Issue.

AB cf. CA 54, 10970c; 55, 6453h. The AcCHNaCO₂Et from 13 g. AcCH₂CO₂Et and 2.3 g. Na in dioxane was treated over 1 hr. with 23.4 g. 2-phenyl-1,4-naphthoquinone in dioxane with ice-cooling, the mixture kept 1 hr. at room temperature, 20 ml. H₂O added, a stream of air blown through the mixture 1.5 hrs., the mixture quenched in ice-HCl, and extracted with Et₂O to give 30% Et 2-phenyl-1,4-naphthoquinon-3-ylacetoacetate, m. 121-3°, and 5% Et₂O-insol. I, m. 182-4°. No products of the latter type were isolated from the subsequent reactions. If the above mixture was heated with 98% AcOH containing a trace of H₂SO₄ 1.5 hrs., the product was 61% 2-methyl-3-carbethoxy-4-phenyl-5-hydroxynaphthofuran (Ia), m. 122-4°. Condensation of AcCH₂CO₂Et or BzCH₂CO₂Et with the appropriate 2-aryl-1,4-naphthoquinone as above gave: Et 2-(p-nitrophenyl)-1,4-naphthoquinon-3-ylacetoacetate, m. 195-7°, 52%; Et 2-phenyl-1,4-naphthoquinon-3-ylbenzoylacetate (II), m. 130-2°, 40%; Et 2-(p-nitrophenyl)-1,4-naphthoquinon-3-ylbenzoylacetate, m. 209-10°, 45%; Et 2-phenyl-1,4-naphthoquinon-3-yl(p-nitrobenzoyl)acetate, m. 138-40°, 55%; Et 2-phenyl-1,4-naphthoquinon-3-yl(p-chlorobenzoyl)acetate, m. 133-5°, 37%. II with aqueous Na₂S₂O₄ gave 88% 2,4-diphenyl-3-carbethoxy-5-hydroxynaphthofuran, m. 128-9°; similarly was prepared 87% 2-(p-nitrophenyl)-3-carbethoxy-4-phenyl-4-hydroxynaphthofuran, m. 226-8°. To AcCHNaCO₂Et, from 22 g. ester, prepared in absolute EtOH, was added at 0° 11.7 g. 2-phenyl-1,4-naphthoquinone in dry dioxane, followed by 20 ml. H₂O, and the whole kept 1 hr. at 50° to yield after acidification 65% I. Reaction of malonic ester with Na in dioxane, followed by treatment with 2-phenyl-1,4-naphthoquinone, as above, gave 50% 2,5-dihydroxy-4-phenyl naphthofuran, m. 195-7°. Shaking Ia with 2N NaOH and Me₂SO₄ in dioxane 1 hr. gave 95% 5-methoxy analog (III) of Ia, m. 122-3°. Similarly was prepared 2,4-diphenyl-3-carbethoxy-5-methoxynaphthofuran m. 106-7°, and 2-(p-nitrophenyl)-3-carbethoxy-4-phenyl-5-methoxynaphthofuran, m. 201-2°. III refluxed with alc. NaOH 4 hrs. gave on acidification 2-methyl-3-carboxy-4-phenyl-5-methoxynaphthofuran, m. 214-16°, which treated with SOCl₂ in CCl₄ at 40° then AlCl₃ at 0° 1 hr. and at room temperature 3 hrs. gave after quenching in ice-HCl 30% IV, m. 174-6°.

L15 ANSWER 1 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2005:17776 CAPLUS

DOCUMENT NUMBER: 143:60031

TITLE: Dialkylphosphinoimidazoles as new ligands for palladium-catalyzed coupling reactions of aryl chlorides

AUTHOR(S): Harkal, Surendra; Rataboul, Franck; Zapf, Alexander; Fuhrmann, Christa; Riermeier, Thomas; Monsees, Axel; Beller, Matthias

CORPORATE SOURCE: Leibniz-Institut fuer Organische Katalyse, Universitaet Rostock e.V., Rostock, 18055, Germany

SOURCE: Advanced Synthesis & Catalysis (2004), 346(13-15), 1742-1748

CODEN: ASCAF7; ISSN: 1615-4150

PUBLISHER: Wiley-VCH Verlag GmbH & Co. KGaA

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 143:60031

AB 1-Aryl-2-(dialkylphosphino)-1H-imidazoles and -benzimidazoles were prepared and examined as ligands for palladium-catalyzed Suzuki coupling of aryl chlorides with phenylboronic acid. Imidazolylphosphines 1-Ar-2-PR₂-1H-imidazoles (1, 2, Ar = 2,4,6-Me₃C₆H₂, R = cyclohexyl, tBu) and 1-Ar-2-(PtBu₂)-1H-benzimidazoles (3, 4; Ar = Ph, 1-naphthyl) were conveniently prepared in one step from the corresponding heterocycles by selective deprotonation and quenching with corresponding ClPR₂. The novel ligands are easily tunable and show good to excellent performance in palladium-catalyzed Suzuki reactions of Ar₁Cl (Ar₁ = 4-MeC₆H₄, 4-MeCOC₆H₄, 4-CF₃C₆H₄, 4-MeOC₆H₄, 3-MeOC₆H₄, 2-MeC₆H₄, 2,6-Me₂C₆H₃, 3-pyridinyl) with phenylboronic acid, affording the corresponding biphenyls with 85-99% yield and 1900-8500 TON values. Buchwald-Hartwig amination of aryl substituted chlorobenzenes and 3-chloropyridine by primary and secondary aliphatic and aromatic amines gave corresponding arylamines with 68-99% yields.

REFERENCE COUNT: 71 THERE ARE 71 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 2 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2004:912880 CAPLUS

DOCUMENT NUMBER: 142:74399

TITLE: Dearomatizing rearrangements of lithiated thiophenecarboxamides

AUTHOR(S): Clayden, Jonathan; Turnbull, Rachel; Helliwell, Madeleine; Pinto, Ivan

CORPORATE SOURCE: Department of Chemistry, University of Manchester, Manchester, M13 9PL, UK

SOURCE: Chemical Communications (Cambridge, United Kingdom) (2004), (21), 2430-2431

CODEN: CHCOFS; ISSN: 1359-7345

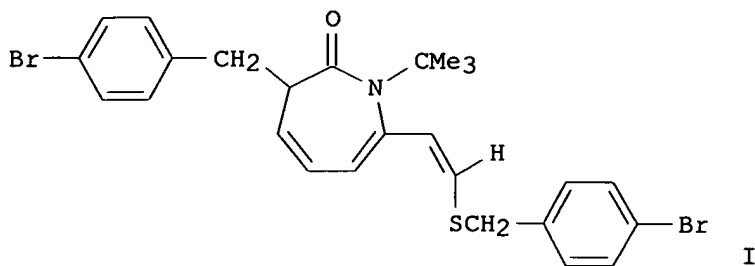
PUBLISHER: Royal Society of Chemistry

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 142:74399

GI



AB Thiophene-3-carboxamides bearing allyl or benzyl substituents at nitrogen undergo dearomatizing cyclization on treatment with LDA. Rearrangements transform the dearomatized products into pyrrolinones, azepinones or partially saturated azepinothiophenes. E.g., deprotonation of N-allyl-N-tert-butylthiophene-3-carboxamide, followed by quenching with p-bromobenzyl bromide, gave 50% azepinone I.

REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 3 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2004:907016 CAPLUS

DOCUMENT NUMBER: 143:115215

TITLE: Polyazapodands derived from biphenyl. Study of their behavior as conformationally regulated fluorescent sensors

AUTHOR(S): Costero, Ana M.; Sanchis, Joaquin; Gil, Salvador; Sanz, Vicente; Ramirez de Arellano, M. Carmen; Gareth Williams, J. A.

CORPORATE SOURCE: Departament de Quimica Organica, Universitat de Valencia, Burjassot, 46100, Spain

SOURCE: Supramolecular Chemistry (2004), 16(6), 435-446
CODEN: SCHEER; ISSN: 1061-0278

PUBLISHER: Taylor & Francis Ltd.

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 143:115215

AB Eight new polyazapodands containing a 4,4'-substituted biphenyl moiety have been synthesized. Four are functionalized on positions 4 and 4' with a nitro group and four with a dimethylamino substituent. Comparison of the emission behavior of clearly suggests that a modification in the dihedral angle between the biphenyl rings is an important factor in determining the fluorescent response of the mol. The fluorescence is pH dependent, due to the formation of intramol. hydrogen bonds between protonated aliphatic nitrogens and a carbonyl oxygen, which influences the aforementioned dihedral angle. A crystal structure resolved by X-ray diffraction, and confirms the dependence of the angle and the rigidity on the hydrogen bonding. The complexation properties of these ligands have been studied with Zn²⁺, Cd²⁺, Ni²⁺, Cu²⁺ and Pb²⁺, which show that the number of amino groups within the pendants has a strong influence on the nature of the complexation and the fluorescent response of each ligand.

REFERENCE COUNT: 20 THERE ARE 20 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 4 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2003:753346 CAPLUS

DOCUMENT NUMBER: 139:364494

TITLE: Photohydration and Photosolvolysis of Biphenyl Alkenes and Alcohols via Biphenyl Quinone Methide-type Intermediates and Diarylmethyl Carbocations

AUTHOR(S): Brousmiche, Darryl W.; Xu, Musheng; Lukeman, Matthew;

Wan, Peter
CORPORATE SOURCE: Department of Chemistry, University of Victoria,
Victoria, BC, V8W 3V6, Can.
SOURCE: Journal of the American Chemical Society (2003),
125(42), 12961-12970.
CODEN: JACSAT; ISSN: 0002-7863
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 139:364494

AB Evidence is presented for the photochem. generation of novel biphenyl quinone methide (BQM)-type intermediates on photolysis of hydroxybiphenyl alkenes 7 and 8 [$\text{PhC}(\text{:CH}_2)\text{C}_6\text{H}_4\text{-4-}$ and $\text{-3-C}_6\text{H}_4\text{OH-4,}$ resp.] and hydroxybiphenyl alcs. 9 and 10 [$\text{PhCOH(Me)C}_6\text{H}_4\text{-4-}$ and $\text{-3-C}_6\text{H}_4\text{OH-4,}$ resp.]. Mechanistic investigations utilizing product, fluorescence, and nanosecond laser flash photolysis (LFP) studies indicate two distinct pathways for the formation of these BQMs depending upon the functional groups of the progenitor. Formal excited-state intramol. proton transfer (ESIPT) between the phenol and the alkene led to BQMs upon irradiation of the hydroxybiphenyl alkenes 7 and 8, while excited-state proton transfer (ESPT) to solvent followed by dehydroxylation was responsible for BQM formation from the hydroxybiphenyl alcs. 9 and 10. Photolysis of 7 and 8 in aqueous CH_3CN gave photohydration products via attack of water on the resp. BQMs, while photolysis of the analogous Me ethers (of the phenolic moiety) gave only carbocation intermediates. Hydroxybiphenyl alcs. 9 and 10 yielded the corresponding photomethanolysis products in aqueous methanol, through attack of CH_3OH on the resp. BQMs. Although no evidence was found for BQM formation in LFP studies of 8 and 10, due to its suspected short lifetime, the resp. diaryl carbocation (λ_{max} 420 nm, $\tau = 8.5$ μs) has been observed upon irradiation of 8 in 2,2,2-trifluoroethanol. A BQM (λ_{max} 580 nm) was observed for 9 but not for 10, the latter having more complex chemical on laser excitation, resulting in a transient that appears to mask any BQM absorption. Significant quenching of fluorescence from the hydroxybiphenyl alkenes at low water content implies that H_2O is directly involved in reaction from the singlet excited state. The decrease in fluorescence intensity of 8 was found to depend on $[\text{H}_2\text{O}]^3$; however, the distance required for ESIPT in these systems is too large to be bridged by a water trimer. The nonlinear quenching has been attributed to deprotonation of the phenol by two water mols., with concerted protonation at the alkene by another mol. of water. Fluorescence quenching of the hydroxybiphenyl alcs. required much higher water content, implying a different mechanism of reaction, consistent with the proposal of ESPT (to solvent water) followed by dehydroxylation.

REFERENCE COUNT: 36 THERE ARE 36 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 5 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2003:170641 CAPLUS
DOCUMENT NUMBER: 138:320857
TITLE: Host-[2]Rotaxane: Advantage of Converging Functional Groups for Guest Recognition
AUTHOR(S): Smukste, Inese; House, Brian E.; Smithrud, David B.
CORPORATE SOURCE: Department of Chemistry, University of Cincinnati,
Cincinnati, OH, 45221-0172, USA
SOURCE: Journal of Organic Chemistry (2003), 68(7), 2559-2571
CODEN: JOCEAH; ISSN: 0022-3263
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 138:320857

AB A host-[2]rotaxane was constructed by converting a diaminophenylcalix[4]arene into a [2]rotaxane using the DCC-rotaxane

method (Zehnder, D.; Smithrud, D. B.; Organic Lett. 2001, 16, 2485-2486). N-Ac-Arg groups were attached to the dibenzo-24-crown-8 ring of the rotaxane to provide a convergent functional group. To demonstrate the advantage provided by the rotaxane architecture for recognition of guests that contain a variety of functional groups, association consts. (KA) for N-Ac-Trp, indole, N-Ac-Gly, fluorescein, 1-(dimethylamino)-5-naphthalenesulfonate, and pyrene bound to the [2]rotaxane were determined by performing ¹H NMR and fluorescence spectroscopic expts. The host-[2]rotaxane had the highest affinity for fluorescein with a KA = 4.6 + 106 M⁻¹ in a 98/2 buffer (1 mM phosphate, pH 7)/DMSO solution. A comparison of KA values demonstrates that both the aromatic pocket and ring of the host-[2]rotaxane contribute binding free energy for complexation. Association consts. were also derived for the same guests bound to the diaminophenylcalix[4]arene and to a diphenylcalix[4]arene that contained arginine residues displayed in a nonconvergent fashion. The host-[2]rotaxane provides higher affinity and specificity for most guests than the host with divergent N-Ac-Arg groups or the one that only has an aromatic pocket. For example, the KA for the complex of the host-[2]rotaxane and fluorescein in the DMSO/water mixture is more than 2 orders of magnitude greater than association consts. derived for the other hosts.

REFERENCE COUNT: 55 THERE ARE 55 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 6 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2002:289507 CAPLUS

DOCUMENT NUMBER: 137:78680

TITLE: Stable ion and electrophilic chemistry of fluoranthene-PAHs

AUTHOR(S): Laali, Kenneth K.; Okazaki, Takao; Galembeck, Sergio E.

CORPORATE SOURCE: Department of Chemistry, Kent State University, Kent, OH, 44242, USA

SOURCE: Journal of the Chemical Society, Perkin Transactions 2 (2002), (3), 621-629
CODEN: JCSPGI; ISSN: 1472-779X

PUBLISHER: Royal Society of Chemistry

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 137:78680

AB The first examples of persistent carbocations derived from parent fluoranthene (four fused rings), benz[e]acephenanthrylene (benzo[b]fluoranthene) (five fused rings) and its C-10 substituted derivs. (X = OMe, F), as well as indeno[1,2,3-cd]pyrene (six fused rings) by protonation with FSO₃H-SO₂ClF are reported. NMR characteristics (500 MHz) of the resulting carbocations, their charge delocalization mode and tropicity are examined. Relative arenium ion energies for all possible protonation sites were calculated by AM1 for comparison with the NMR-based assignments. The NMR chemical shifts for the observed arenium cations were computed by GIAO-DFT calcs. at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level (their energies and those of their neutral precursors were also calculated at this level of theory). Relative aromaticity in various rings in the resulting PAH-arenium ions was gauged via nucleus independent chemical shift (NICS) calcs. It has been shown that the site of protonation and nitration in 10-methoxybenz[e]acephenanthrylene are the same (C-9). Quenching of the superacid solns. of fluoranthene and 10-methoxybenz[e]acephenanthrylene produced the dimers 3,3'-bifluoranthenyl and 10,10'-dimethoxy-9,9'-biacephenanthrenyl as minor products (ca. 10% and ca. 33% resp.) in addition to the intact PAHs. It has also been demonstrated that fluoranthene-PAHs and their derivs. are easily protonated with [NH₄][NO₃] and observed in the gas phase via electrospray mass spectrometry (ES-MS).

REFERENCE COUNT: 40 THERE ARE 40 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 7 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 2001:475265 CAPLUS
DOCUMENT NUMBER: 135:235356
TITLE: Metallocyclodextrins as Building Blocks in Noncovalent Assemblies of Photoactive Units for the Study of Photoinduced Intercomponent Processes
AUTHOR(S): Haider, Johanna M.; Chavarot, Murielle; Weidner, Steffen; Sadler, Ian; Williams, Rene M.; De Cola, Luisa; Pikramenou, Zoe
CORPORATE SOURCE: School of Chemistry, The University of Birmingham, Edgbaston Birmingham, B15 2TT, UK
SOURCE: Inorganic Chemistry (2001), 40(16), 3912-3921
CODEN: INOCAJ; ISSN: 0020-1669
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 135:235356

AB Cyclodextrin cups were employed to build supramol. systems consisting of metal and organic photoactive/redox-active components; the photoinduced communication between redox-active units assembled in H₂O via noncovalent interactions is established. The functionalization of a β -cyclodextrin with a terpyridine unit, ttp- β -CD, is achieved by protection of all but one of the hydroxyl groups by methylation and attachment of the ttp unit on the free primary hydroxyl group. The metalloreceptors [(β -CD-ttp)Ru(ttp)][PF₆]₂, [(β -CD-ttp)Ru(tpy)][PF₆]₂, and [Ru(β -CD-ttp)2][PF₆]₂ were synthesized and fully characterized. The [(β -CD-ttp)Ru(ttp)][PF₆]₂ metalloreceptor exhibits luminescence in H₂O, centered at 640 nm, from the 3MLCT state with a lifetime of 1.9 ns and a quantum yield of $\Phi = 4.1 \times 10^{-5}$. Addition of redox-active quinone guests AQS, AQC, and BQ to an aqueous solution of [(β -CD-ttp)Ru(ttp)]₂⁺ results in quenching of the luminescence up to 40%, 20%, and 25%, resp. Measurement of the binding strength indicates that, in saturation conditions, 85% for AQS and 77% for AQC are bound. The luminescence quenching is attributed to an intercomponent electron transfer from the appended Ru center to the quinone guest inside the cavity. Control expts. demonstrate no bimol. quenching at these conditions. A photoactive Os metalloguest, [Os(biptpy)(tpy)][PF₆], is designed with a biphenyl hydrophobic tail for insertion in the cyclodextrin cavity. The complex is luminescent at room temperature with an emission band maximum at 730 nm and a lifetime of 116 ns. The Os(III) species are formed for the study of photoinduced electron transfer upon their assembly with the Ru cyclodextrin, [(β -CD-ttp)Ru(ttp)]₂⁺. Time-resolved spectroscopy studies show a short component of 10 ps, attributed to electron transfer from Ru(II) to Os(III) giving an electron transfer rate 9.5×10^9 s⁻¹.

REFERENCE COUNT: 72 THERE ARE 72 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 8 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1985:148586 CAPLUS
DOCUMENT NUMBER: 102:148586
TITLE: Photophysical studies on 1-(p-aminophenyl)pyrene. Characterization of an intramolecular charge-transfer state with application to proton-transfer dynamics
AUTHOR(S): Hagopian, Sair; Singer, Lawrence A.
CORPORATE SOURCE: Dep. Chem., Univ. South. California, Los Angeles, CA, 90089-1062, USA
SOURCE: Journal of the American Chemical Society (1985), 107(7), 1874-80
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal

LANGUAGE: English
OTHER SOURCE(S): CASREACT 102:148586

AB A photophys. study on 1-(p-aminophenyl)pyrene (I) reveals 2 principal fluorescences arising from π, π^* (locally excited in pyrene ring) and charge-transfer (CT) (PhNH₂ as donor, pyrene as acceptor) states. The latter of the CT states in highly polar solvents (.apprx.500 nm, .apprx.2.5 eV) agrees well with the measured redox energetics (2.7 eV) while the dependence of the transition of .apprx.14 D. The photophysics of I is pH dependent in aqueous media because of conjugate acid-base equilibrium, with ground- and excited-state consts. of pK_a = 4.05, pK_a^{*} = 3.3 (Forster cycle), resp., in 1:1 EtOH-H₂O. The rather similar acidities of the ground and excited states of I indicate little or no CT contribution to the excited-state deprotonation. Deprotonation of the locally excited π, π^* state of I conjugate acid yields initially the locally excited free-base form of I, which rapidly relaxes to the CT state. The latter is subject to proton-transfer quenching (most likely via the pyrene radical-anion moiety of the CT state), k_q = (7.38 ± 1.5) × 10⁸ M⁻¹ s⁻¹ (corrected for changing proton activity coeffs. in EtOH-H₂O). Study of the rate of deprotonation of the conjugate acid of I^{*} from room temperature through the liquid-solid phase transition (near -50°) to -196° allows an estimate of the enthalpy and entropy of activation in several different regions. As the temperature is lowered from 295 to 160 K, the enthalpy term decreases from 5360 to 780 cal/mol while the entropy term changes from -6.1 to -24.3 cal/K·mol).

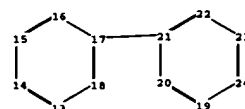
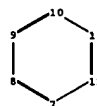
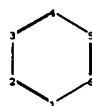
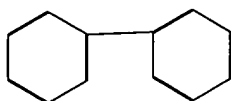
L15 ANSWER 9 OF 9 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1961:43315 CAPLUS
DOCUMENT NUMBER: 55:43315
ORIGINAL REFERENCE NO.: 55:8429e-i, 8430a-c
TITLE: Quinones. XXXIII. Condensation of aryl naphthoquinones with sodium enolates of acetoacetic and malonic esters and their analogs
AUTHOR(S): Grinev, A. N.; Mezentshev, A. S.; Terent'ev, A. P.
CORPORATE SOURCE: State Univ., Moscow
SOURCE: Zhurnal Obshchei Khimii (1960), 30, 2306-11
CODEN: ZOKHA4; ISSN: 0044-460X
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 55:43315

GI For diagram(s), see printed CA Issue.

AB cf. CA 54, 10970c; 55, 6453h. The AcCHNaCO₂Et from 13 g. AcCH₂CO₂Et and 2.3 g. Na in dioxane was treated over 1 hr. with 23.4 g. 2-phenyl-1,4-naphthoquinone in dioxane with ice-cooling, the mixture kept 1 hr. at room temperature, 20 ml. H₂O added, a stream of air blown through the mixture 1.5 hrs., the mixture quenched in ice-HCl, and extracted with Et₂O to give 30% Et 2-phenyl-1,4-naphthoquinon-3-ylacetoacetate, m. 121-3°, and 5% Et₂O-insol. I, m. 182-4°. No products of the latter type were isolated from the subsequent reactions. If the above mixture was heated with 98% AcOH containing a trace of H₂SO₄ 1.5 hrs., the product was 61% 2-methyl-3-carbethoxy-4-phenyl-5-hydroxynaphthofuran (Ia), m. 122-4°. Condensation of AcCH₂CO₂Et or BzCH₂CO₂Et with the appropriate 2-aryl-1,4-naphthoquinone as above gave: Et 2-(p-nitrophenyl)-1,4-naphthoquinon-3-ylacetoacetate, m. 195-7°, 52%; Et 2-phenyl-1,4-naphthoquinon-3-ylbenzoylacetate (II), m. 130-2°, 40%; Et 2-(p-nitrophenyl)-1,4-naphthoquinon-3-ylbenzoylacetate, m. 209-10°, 45%; Et 2-phenyl-1,4-naphthoquinon-3-yl(p-nitrobenzoyl)acetate, m. 138-40°, 55%; Et 2-phenyl-1,4-naphthoquinon-3-yl(p-chlorobenzoyl)acetate, m. 133-5°, 37%. II with aqueous Na₂S₂O₄ gave 88% 2,4-diphenyl-3-carbethoxy-5-hydroxynaphthofuran, m. 128-9°; similarly was prepared 87% 2-(p-nitrophenyl)-3-carbethoxy-4-phenyl-4-hydroxynaphthofuran, m. 226-8°. To AcCHNaCO₂Et, from 22 g. ester, prepared in absolute EtOH, was

added at 0° 11.7 g. 2-phenyl-1,4-naphthoquinone in dry dioxane, followed by 20 ml. H₂O, and the whole kept 1 hr. at 50° to yield after acidification 65% I. Reaction of malonic ester with Na in dioxane, followed by treatment with 2-phenyl-1,4-naphthoquinone, as above, gave 50% 2,5-dihydroxy-4-phenylnaphthofuran, m. 195-7°. Shaking Ia with 2N NaOH and Me₂SO₄ in dioxane 1 hr. gave 95% 5-methoxy analog (III) of Ia, m. 122-3°. Similarly was prepared 2,4-diphenyl-3-carbethoxy-5-methoxynaphthofuran m. 106-7°, and 2-(p-nitrophenyl)-3-carbethoxy-4-phenyl-5-methoxynaphthofuran, m. 201-2°. III refluxed with alc. NaOH 4 hrs. gave on acidification 2-methyl-3-carboxy-4-phenyl-5-methoxynaphthofuran, m. 214-16°, which treated with SOCl₂ in CCl₄ at 40° then AlCl₃ at 0° 1 hr. and at room temperature 3 hrs. gave after quenching in ice-HCl 30% IV, m. 174-6°.



ring nodes :

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24

chain bonds :

17-21

ring bonds :

1-2 1-6 2-3 3-4 4-5 5-6 7-8 7-12 8-9 9-10 10-11 11-12 13-14 13-18 14-15 15-16 16-17
17-18 19-20 19-24 20-21 21-22 22-23 23-24

exact bonds :

17-21

normalized bonds :

1-2 1-6 2-3 3-4 4-5 5-6 7-8 7-12 8-9 9-10 10-11 11-12 13-14 13-18 14-15 15-16 16-17
17-18 19-20 19-24 20-21 21-22 22-23 23-24

Match level :

1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom 11:Atom 12:Atom
13:Atom 14:Atom 15:Atom 16:Atom 17:Atom 18:Atom 19:Atom 20:Atom 21:Atom 22:Atom 23:Atom
24:Atom

fragments assigned product role:

containing 13

fragments assigned reactant/reagent role:

containing 1

containing 7